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*Stephen Hordley*

Dated

16 July 2004

12 FEB 2004

NEWPORT



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13FEB04 E872877-1 002914  
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1. Your reference MSP640 GB2
  
2. Patent application number 0403131.6  
(The Patent Office will fill this part in) 12 FEB 2004
  
3. Full name, address and postcode of the or of each applicant (underline all surnames) Dow Corning Ireland Limited  
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Patents ADP number (if you know it)  
  
If the applicant is a corporate body, give the country/state of its incorporation
  
4. Title of the invention  
  
Functionalisation of Particles
  
5. Name of your agent (if you have one) A M Donlan  
  
"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode) Dow Corning Limited  
Intellectual Property Department  
Cardiff Road  
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Patents ADP number (if you know it) 414037001
  
6. Priority: Complete this section if you are declaring priority from one or more earlier patent applications, filed in the last 12 months.

Country	Priority application number (if you know it)	Date of filing (day / month / year)
  
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Number of earlier UK application	Date of filing (day / month / year)
  
8. Is a Patents Form 7/77 (Statement of inventorship and of right to grant of a patent) required in support of this request? Yes  
Answer YES if:  
a) any applicant named in part 3 is not an inventor, or  
b) there is an inventor who is not named as an applicant, or  
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Otherwise answer NO (See note d)

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9. Accompanying documents: A patent application must include a description of the invention. ~~Not counting duplicates, please enter the number of pages of each item accompanying this form:~~

Continuation sheets of this form

Description

32 /

Claim(s) 5 /

Abstract

Drawing(s) 2

12 June

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)


Request for a preliminary examination and search (Patents Form 9/77)

Request for a substantive examination (Patents Form 10/77)

Any other documents (please specify)

11. I/We request the grant of a patent on the basis of this application.

Signature(s) A M Donlan



Date 12/02/04

12. Name, daytime telephone number and e-mail address, if any, of person to contact in the United Kingdom

A M Donlan 01446-723740

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## FUNCTIONALISATION OF PARTICLES

[0001] The present application describes a process for the surface activation and/or surface functionalisation of particles using excited and/or unstable gas processes that can be scaled-up for industrial production.

[0002] The need to compatibilise, or disperse inorganic and organic particles into product compositions is a major concern in many industries. This may, for example, be due to major difficulties in achieving acceptable particle dispersion, a factor which is often determined at least partially by the size of the particles and their surface chemistry. The surface chemistry of most solids, liquids or gel-like particles are determined by the manufacturing processes concerned. Furthermore, often after preparation particles can be stored for a long time before use and during this period there is a tendency for agglomeration to occur which can result in a change to their overall surface properties.

[0003] Even when a dispersion step is successfully completed the particles may need appropriate chemical functionalities to interact or bind to a matrix such as a polymeric, polymerisable and/or cross-linkable material. The need to specifically functionalise a solid substrate with an organic group bearing a chemical functionality compounds the problems regarding dispersability and is a widespread problem for many industrial process and can lead to the need for complicated processes merely to render particles suitable for dispersion or the like. Problems are particularly seen for example in the case of active biomolecules (e.g. enzymes) where it is important to attach the biomolecules to a substrate without impairing the biological activity.

[0004] Another problem is a need for the passivation of inorganic powdered pigments in order to avoid skin irritation and other such problems in medical and toiletry type products. An example for the need of passivation is in the recycling industry for rubbers and plastics, for example in the automotive sector to achieve mechanical performances matching those of new polymer based products for minimal cost. Examples may include the recycling of natural and synthetic SBR rubber from tyres, and the recycling of ethylene propylene diene methylene (EPDM) and/or polypropylene from various parts in cars. The concept of

improved mechanical performance and commercialisation possibility must be confirmed. It is noteworthy that the recycling industry also targets other plastic materials such as polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET), EPDM and the like. Various groups in the world have looked at ways of recycling tyre rubber.

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[0005] Current recycling approaches for tyre rubber generally involve the incorporation of rubber particles (commonly referred to as "rubber crumb") into a polymer matrix to form composites. Usually, the mechanical properties of such composites are not high performance because of the low surface energy or low chemical reactivity of the organic surface.

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[0006] Plasma is an at least partially ionised gaseous medium, made of excited, unstable and ionised atoms and molecules and emits visible and UV radiation. When matter is continually supplied with energy, its temperature increases and it typically transforms from a solid to a liquid and, then, to a gaseous state. Continuing to supply energy causes the system to undergo yet a further change of state in which neutral atoms or molecules of the gas are broken up by energetic collisions to produce negatively charged electrons, positive or negatively charged ions. Other species resulting from plasma treatment of a gas include high energy non-charged particles such as gas molecules in excited states, metastable compounds, molecular fragments and or radicals. This mix of excited and charged particles exhibiting collective behaviour is called "plasma", the fourth state of matter. The plasma is electrically neutral and therefore contains positive ions, negative ions and electrons such that the algebraic sum of their charges is zero. The plasma phase is obtained in the laboratory by subjecting a pure gas or a gaseous mixture to external excitation, which is most generally electrical.

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[0007] The term "plasma" covers a huge range of systems whose density and temperature vary by many orders of magnitude. Some plasmas are very hot and all their microscopic species (ions, electrons, etc.) are in approximate thermal equilibrium, the energy input into the system being widely distributed through atomic/molecular level collisions; examples include flame based plasmas. Other plasmas, however, particularly those at low pressure (e.g. 100 Pa) where collisions are relatively infrequent, have their constituent species at widely different temperatures and are called "non-thermal non-equilibrium" plasmas.

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[0008] In these non-thermal non-equilibrium plasmas, the free electrons are very hot with temperatures of many thousands of Kelvin (K) whilst the neutral and ionic species remain cool. Because the free electrons have almost negligible mass, the total system heat content is low and the plasma operates close to room temperature thus allowing the processing of temperature sensitive materials, such as plastics or polymers, without imposing a damaging thermal burden. The hot electrons create, through high energy collisions, a rich source of radicals and excited and/or unstable species with a high chemical potential energy capable of profound chemical and physical reactivity. It is this combination of low temperature operation plus high reactivity which makes non-thermal equilibrium plasma technologically important and a very powerful tool for manufacturing and material processing as it is capable of achieving processes which, if achievable at all without plasma, would require very high temperatures or noxious and aggressive chemicals.

[0009] Because of their potential in industrial applications atmospheric pressure plasma (APP) systems are of particular interest to industry. APP is a form of atmospheric pressure non-equilibrium plasma and is generated between two parallel electrodes that vary in sizes and configurations but which need to be within several mm distance from each other. Depending on the electrical circuitry and on systems configurations, atmospheric pressure glow discharge (APGD) and/or dielectric barrier discharge (DBD) plasmas are generally produced. Advantageously, when compared to many plasma-based systems currently available, APP operates at about atmospheric pressure and at low temperatures low temperatures ( $<200^{\circ}\text{C}$  and preferably  $<100^{\circ}\text{C}$ ). However, limitations exist with respect to system geometry, because the plasma is produced in a plasma region between parallel electrodes with very small gaps between electrodes. It is ideally suited to treat flat, thin and flexible substrates like plastic films, textile webs, etc.

[0010] In the case of the preparation of powders using APGD type processes, one problem regarding the geometry of the system is that during the generation of the particles, reacted reagents and/or treated particles may deposit on the electrodes thereby affecting the electrical and chemical properties of the plasma and potentially the duration of usefulness of the electrodes. Furthermore, the use and or preparation of electrically conducting particles

using APGD is difficult as such particles would interact with the electrical field and create filaments or local discharges and potentially adhere to electrode surfaces.

5 [0011] Recently, new plasma system have been developed which produce plasmas using high gas flows between the electrodes of an electrical system. These gases exit the system in the form of excited and/or unstable gas mixtures at around atmospheric pressure. These gas mixtures are characterized by being substantially free of electrical charged species which may be utilized in downstream applications distant from the gap between the electrodes which generates the plasma. This "atmospheric pressure post plasma" (APPP) has some of the  
10 physical characteristics of low pressure glow discharge and APGD including, for example, glow, presence of active light emitting species, chemical reactivity. However, some clear and unique differences exist including the facts that APPP has higher thermal energy, absence of boundary walls e.g. no electrodes, substantial absence of electrically charged species, large choice of gases and mixture of gases, large flow rate of gases.

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[0012] US5807615 describes a "post discharge" atmospheric pressure plasma system for depositing e.g. silicon oxide films on metal substrates wherein a "primary" gas is excited by being passed through a plasma and is then mixed with a precursor gas downstream of the plasma. The precursor gas was a silicon containing compound which has not been plasma  
20 treated. The precursor gas was excited by interaction with the primary gas resulting in the formation of a film on a substrate surface. The post discharge nature of this system resulted in the substantial absence of any electrically charged species other than in the plasma region between the electrodes. Column 3 lines 33- 40 states that "since the silicon precursor gas has not passed through the apparatus the risk of forming silica powder (or more generally  
25 powders of silicon compounds) inside the plasma discharge is consequently eliminated."

[0013] The treatment of powdered substrates using atmospheric pressure plasma has been previously described. In JP 06-000365 there is provided an apparatus for continuously plasma treating a powdered substrate by coaxially pivoting a metallic inner and outer  
30 cylinders at least one side of the outer cylinder being coated with a dielectric to form a fixed gap between the cylinders, inclining the cylinders and passing a voltage across the electrodes to effect the atmospheric pressure plasma treatment of a powdered substrate. In JP 06-

228739 there is provided a means for surface treating a powdered substrate by atmospheric-pressure glow discharge by gas floating the powdered substrate with a rare gas or mixture of a rare gas and a gaseous reactant. The treatment occurs in a substantially cylindrical vertical positioned reaction vessel at the bottom of which gas is introduced to float the powdered substrate and the exit is out of the top of the vessel carried by the gas having been first subjected to and atmospheric-pressure glow discharge at a pressure higher than atmospheric pressure. In US5399832 there is provided a method for treating and/or coating an organic or inorganic powdered substrate using an organic monomer with atmospheric pressure glow discharge.

[0014] In WO 97/29156 there is provided a method of treating deagglomerated particles with plasma activated gas to modify the surface of the particles and species. EP 0655516 describes the coating/surface treatment of solid particles using a plasma fluidised bed in which a plasma is generated outside the fluidised bed using a gaseous coating material and a carrier gas which excited mixture is subsequently introduced into the fluidised bed for coating particles. Leroy et.al., have described a process involving the treatment of a polyethylene powder using a remote nitrogen plasma reactor coupled with a fluidised bed in Plasmas and Polymers 8(1) 2003 p 13 – 29. Mori et al describe the development of silica coating methods for powdered pigments with atmospheric pressure glow plasma in Thin Solid films 316(1,2) 1998 p 89 – 92 and Ogawa et al. describe the preparation of zirconia coatings on amorphous magnetic powder by atmospheric pressure glow plasma in Thin Solid Films 386(2) 2001 p 213 – 216. US 6428861 describes a system for treating particulate matter in a continuous or semi-continuous mode at sub-atmospheric pressure. Quede et al., (J. Materials Sci., 37, 2002 p 1395 – 9) have described a cold remote nitrogen plasma system used to treat polyamide-6 and polyamide-6 clay nanocomposite powders and subsequently coating them with plasma polymerised 1,2,3,3-tetramethyldisiloxane. The reactor was used to deposit the coating on the polymer powders in a fluidised bed reactor. US 6241858 describes a vacuum plasma process for coating a thin film onto powdered substrates.

[0015] All of the aforementioned prior art generally relates to the activation of the powdered substrate or applications of coatings using gas phase precursors and typically the



results suggest low deposition rates and require high residence times to obtain a sufficiently coated surface.

[0016] WO 02/28548 describes a process for enabling the introduction of a solid or liquid precursor into an atmospheric pressure plasma discharge and/or an ionised gas stream resulting therefrom in order to form a coating on a substrate. The substrate may be a powder. WO 03/086030 which was published after the priority date of the present invention describes a method of forming a coating on a powdered substrate within the plasma generated between the electrodes using a process adapted from WO 02/28548.

[0017] In accordance with a first embodiment of the present invention there is provided A method of functionalising a powdered substrate, which method comprises the following steps:-

- i) passing a gas into a means for forming excited and/or unstable gas species.;
- ii) treating said gas such that upon leaving said means the gas comprises excited and/or unstable gas species which are substantially free of electric charge; at a temperature below 400°C.
- iii) treating the powdered substrate with said excited and/or unstable gas species and a functionalising precursor both of which have not been subjected to steps (i) and (ii); in a downstream region external to the means for forming excited and/or unstable gas, wherein said functionalising precursor is introduced simultaneously with or subsequent to introduction of the powdered substrate;
- iv) collecting resulting functionalised substrate.

[0018] For the purposes of this application a powder is a solid material in the form of nanoparticles, nanotubes, particles, particulates, pellets, platelets, needles/tubes, flakes, dust, granulates and any aggregates of the aforementioned forms. A gel is typically a jelly-like material in the form of a thin film or solidified mass. It is to be understood that the term "electrically charged species" as used herein is intended to mean ions and electrons.

Functionalisation in accordance with the present invention is to be understood to mean grafting a functional group or compound bearing functional groups onto and/or into a substrate.

Functionalisation may also include coating or encapsulation of the substrate by grafting or covalent bonding with a compound bearing functional groups.

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[0019] The means for forming excited and/or unstable gas species at a temperature of between 10°C and 500°C treats gases passing between the electrodes, which gas upon leaving said means comprises excited and/or unstable gas species which are substantially free of electrical charges. Such excitation is preferably obtained by electrical discharge, for example, of the dielectric barrier discharge type and/or non-thermal equilibrium plasma type.

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However, any other method capable of exciting a gas mixture such as glow discharge and/or dielectric barrier discharge and/or corona discharge, light radiation assisted e.g. laser, and any high energetic means is falling within the scope of this invention. The excited gas mixture is generated in a non-thermal equilibrium plasma and/or dielectric barrier discharge and/or

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corona discharge under approximately atmospheric pressure conditions (e.g. from about  $0.1 \times 10^5$  Pa to about  $3 \times 10^5$  Pa but preferably at a pressure of between from about  $0.5 \times 10^5$  Pa to about  $1.5 \times 10^5$  Pa). Such a means is adapted to provide a post plasma discharge region of excited and/or unstable species downstream from and preferably external to the means for forming excited and/or unstable gas species. Henceforth this region will be referred to as "the

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downstream region". The downstream region is generally substantially free of charged particles. The operating temperature of the means for forming excited and/or unstable gas species is between 10 and 400°C. Preferably the operating temperatures of such apparatus is from about room temperature (i.e. about 20°C) to about 200°C but more preferably, the method of the present invention will operate at temperatures between room temperature (20°

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C) and 160° C. Preferably, gas to be plasma treated has a high flow rate of greater than 50 litres/min, preferably in the range of from 50 litres/min to 500 litres/min, more preferably from about 75 litres/min to 300 litres/min through the means for forming excited and/or unstable gas species.

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[0020] Any equipment suitable for use in producing a downstream region may be used to undertake the method of the present invention. The means for forming the excited and/or unstable gas species may, for example be any means for generating a downstream



region which is preferably substantially free of charged species and which is suitable for use in the method in accordance with the present invention. An Atmospheric Pressure Non-Equilibrium Plasma system, particularly an atmospheric pressure glow discharge having a high gas flow rate (greater than 50 litres per minute) is preferred. Many atmospheric pressure based plasma systems such as glow discharge and dielectric barrier discharge (DBD) based systems typically have low gas flow rate systems (under 50 litres/min) in which the plasma is generated between adjacent electrodes and do not provide a downstream region of the type required in accordance with the present invention and as such are unsuitable for the preparation of particles in accordance with the present invention.

[0021] The means for forming excited and/or unstable gas species may alternatively be a dielectric barrier discharge and/or corona discharge system having a high gas flow rate of at least 50 litres/min so as to provide a suitable downstream region, which is preferably substantially free of charged species for treating the functionalising precursors in accordance with the method of the present invention. Particularly preferred systems include the so-called plasma jet and plasma knife type systems.

[0022] Particularly preferred systems for the present invention are the means for forming excited and/or unstable gas species as described in US 5941448 and/or in the applicant's co-pending application WO 03/085693, when used with a dynamic gas flow. WO 03/085693 was published after the earliest priority date of the present invention.

[0023] The preferred system comprises a concentric cylindrical electrode configuration having an inlet for the introduction of the gas to be excited and an outlet, in the form of a slit, through which excited and/or unstable gas is able to leave the excitation region. The excitation region is substantially the gap between adjacent pairs of concentric electrodes where a plasma is formed and/or dielectric barrier discharge and/or corona discharge occurs. The electrode configuration typically comprises an inner cylindrical electrode and an outer concentric tubular electrode. At least one of the electrodes has a layer of a dielectric material between it and the other electrode. Preferably at least the inner face of the outer electrode is covered with a dielectric material. The slit is provided along most of the axial length of the

electrode configuration in order to provide an elongate source of excited and/or unstable gas in the downstream region into which functionalising precursor is introduced.

[0024] By adding functionalising precursors in the downstream region, which is substantially free of charged species, powdered compounds mixed with functionalising precursor in accordance with the method of present invention may be functionalised.

[0025] In such cases a plume is visible substantially immediately external to the slit which is generally considered to be caused by excited and/or unstable species (atoms and molecules) e.g. metastables, giving off energy when returning to their ground state after having been in the downstream region.

[0026] The geometry of the above electrode configuration means that a system of this type offers unique advantages that allow practical, economic, and large-scale production.

[0027] A typical means for forming excited and/or unstable gas species for use in the method of the present invention may comprise an electrode configuration comprising one or more pairs of concentric electrodes between which a plasma is generated and/or dielectric barrier discharge and/or corona discharge occurs in a substantially constant gap of from 1 to 100mm, preferably from 2 to 10 mm between the electrodes. The electrodes being radio frequency (RF) energised with a root mean square (rms) potential of 1 to 100 kV, preferably between 1 and 30 kV and most preferably between 2.5 and 10 kV, however the actual value will depend on the chemistry/gas choice and plasma region size between the electrodes. The frequency is generally between from 1 to 500 kHz, preferably at 10 to 300 kHz. Preferably, the power used in the apparatus is preferably greater than or equal to  $1 \text{ W/cm}^2$ , more preferably greater than or equal to  $10 \text{ W/cm}^2$  and most preferably will be between from about 10 to about  $100 \text{ W/cm}^2$  (normalised per unit surface area of dielectric).

[0028] Metal electrodes may be used and may be in, for example, the form of metallic cylinders, tubes, plates or mesh. The metal electrodes may be bonded to dielectric material either by adhesive or by some application of heat and fusion of the metal of the electrode to the dielectric material. Alternatively one or more of the electrodes may be encapsulated within a

dielectric material or may be in the form of a dielectric material with a metallic coating such as, for example a dielectric, preferably a glass dielectric with a sputtered metallic coating.

5 [0029] The dielectric materials may be made from any suitable dielectric, examples include but are not restricted to polycarbonate, polyethylene, glass, glass laminates, epoxy filled glass laminates, ceramics and the like.

10 [0030] The gas used to form the excited and/or unstable gas species which are provided to the downstream region need not comprise noble gases such as helium and/or argon and therefore may be solely air, nitrogen, oxygen, hydrogen or the like and any suitable mixture thereof. Where an oxidising or reducing gas is required to be included in the gas used to form the excited and/or unstable gas species, the gas used may comprise a mixture of, for example, 15 NO<sub>2</sub>, or air and nitrogen with an appropriate reducing gas, e.g. H<sub>2</sub>, CH<sub>4</sub> or NH<sub>3</sub> when a reducing plasma environment is required. However, the selection of gas depends upon the plasma processes to be undertaken. Oxidizing or reducing gases will be used alone or in mixtures, typically with nitrogen in any appropriate mixture such as for example in the case of an nitrogen and oxygen mixture, the mixture may comprise 90 – 99.995% nitrogen and 50ppm 20 to 10% oxidizing or reducing gas. The noble gases, Ar, He, Ne, Xe and Kr may be utilised alone or in combination with oxidising or reducing gases (Ar and/or He being the most preferred) but are expensive and as such are only used if needed. Mixtures of any of the above may also be used where deemed appropriate.

25 [0031] Under oxidising conditions, the present method may be used to form an oxygen containing coating on the powdered substrate. For example, silica-based coatings can be formed on the powdered substrate surface from atomised silicon-containing coating-forming materials. Under reducing conditions, the present method may be used to form oxygen free coatings, for example, silicon carbide based coatings may be formed from 30 atomised silicon containing coating forming materials.

[0032] The introduction of the excited and/or unstable gas species into the downstream region is preferably achieved by passing a gas, at a high flow rate (e.g. greater than 50 litres/min), through the electrode configuration of the means for forming excited and/or unstable gas species as described above, which when a potential difference is applied between the electrodes generates a plasma or dielectric barrier discharge and/or corona discharge between adjacent pairs of electrodes. When a plasma is generated between the electrodes, the gap between the electrodes will contain an ionised gaseous medium, comprising excited and ionised atoms and molecules and will emit visible and UV radiation. Gas having passed between the electrodes and out through the slit comprise an excited and/or unstable gas mixture which is substantially free of electrically charged species as substantially all the charged species will remain in the gap between the electrodes. The visible plume which is observed at the slit is the effect of the excited and unstable atoms and molecules giving off energy when returning to their ground state.

[0033] Whilst gases may be excited due to microwave excitation in the method of the present invention, this is not a preferred option.

[0034] The powdered substrate may, be introduced into the downstream region by any suitable means, for example, powder may be introduced by merely being dropped under gravity into or through the downstream region or may be transported therethrough on a support or the like such as on a reel to reel support, conveyor belt or vibrating conveyor. In one preferred embodiment the powder enters the downstream region in a fluidised or circulating bed. A fluidised or circulating bed in the context of the present invention means a process based on fluidized beds of solid particles, in which the solids, by suspension or agitation, exist in an expanded state with zero angle of repose and assume the shape of the containing vessel. Such fluidized beds may also be known as moving bed, aerated beds, self supporting or boiling beds, bubbling beds and turbulent beds, and when the gas superficial velocities are high enough can also become relatively dilute circulating and transport systems. Fluidisation is generally achieved by pneumatic gas velocity means but can also be assisted by mechanical and sonic means known to those skilled in the art. Transport systems suitable for the present invention include the fluidized bed systems described in Perry's Chemical Engineer's handbook 6th Ed, 1984 pages 20-59 to 20-77. Ref fig 20-75.

Alternatively the powdered substrate may be entrained on a carrier gas or transported in a vortex or dual cyclone type apparatus.

[0035] The functionalised precursor is preferably in the form of a liquid and/or gas precursor. For the sake of this invention a liquid shall be understood to mean liquid  
5 compound, a solution of a high viscosity liquid or solid compound in either a liquid carrier or a liquid co-reactive and/or a molten solid. When using a liquid functionalising precursor, the liquid functionalising precursor may be entrained on a carrier gas or transported in a vortex or dual cyclone type apparatus, in which case the liquid to be treated may be fed in through one  
10 or more inlets within e.g. a fluidised bed.

[0036] In one preferred embodiment of the present invention there is provided a single unit comprising the means for forming excited and/or unstable gas species, a powder introduction means for introducing powders to be functionalised into the excited and/or  
15 unstable gas, a functionalising precursor introduction means for introducing functionalising precursors into the excited and/or unstable gas and a suitable means of collecting the end product e.g. by way of an electrostatic precipitator, a cyclone, a scrubber, or filter system or the like. Preferably the means for collecting the end product may be positioned downstream of the excited and/or unstable gas regions, particularly in cases where the resulting product particles  
20 are very fine e.g. nanoparticulate size particles where the particles float in e.g. a fluidized or circulating bed.

[0037] Preferably the single unit is a fluidised or circulating bed reactor. Particularly preferred is a system wherein the means for forming excited and/or unstable gas species is  
25 positioned such that the gas which is used as the source of excited and/or unstable gas species in the downstream region at the base of the fluidised or circulating bed reactor is also utilised as the gas supporting the fluidised or circulating bed. The use of a fluidised or circulating bed type of system results in excellent mixing and thereby a generally consistent product particle size, which may be substantially predetermined by pre-setting the exposure time of the  
30 functionalising precursors in the downstream region of the fluidised or circulating bed. ]  
The functionalised and non-functionalised powder circulating in the fluidised or circulating

bed will be transportable through both the downstream region and where appropriate through the external plume.

[0038] Furthermore, the powdered substrate and/or functionalised precursor may be maintained stationary in a suitable container which may be fixed in the downstream region, in which case, if required, the means for forming excited and/or unstable gas species may be moved relative to the container and the functionalising precursor may be adapted to be introduced directly into the container. Whichever means of transporting and/or retaining the powdered substrate is utilised, it is preferred that the exposure time in which powdered substrate remains within the downstream region is constant in order to ensure an even treatment throughout the duration of the method in accordance with the present invention.

[0039] Additional gas inlets or exits from external gas sources and/or additional means for forming excited and/or unstable gas species may be positioned anywhere in the fluidised or circulating bed e.g. at the bottom, side or top of the reactor, to assist in suspending particles and/or droplets or the like against gravity. Each of said additional means would utilize the source of gas as the gas for the fluidised or circulating bed. A single acoustic self-oscillating jet plasma head may be utilised to offer dynamic mixing/fluidisation in the fluidised or circulating bed as well as forming a plasma between electrodes.

[0040] Preferably, both particles of functionalised and non-functionalised powders which are present in the downstream region in accordance with the present invention (preferably in a fluidised or circulating bed), are prevented by the flow rate of the excited and/or unstable gas entering the fluidised or circulating bed through the slit from passing into the electrode configuration through the exit slit and depositing on one of the electrodes. However where appropriate an electrically conducting mesh may be placed in the fluidised or circulating bed external to the outer electrode, preferably between the external plume and the downstream region. The inclusion of the mesh may serve several purposes, firstly it significantly reduces the opportunity for and preferably prevents particles of functionalised and non-functionalised powders obtained in accordance with the method of the present invention, entering the slit and depositing on an electrode surface. Secondly it also substantially prevents any residual charged species from entering the downstream region and



thirdly it acts as a means of distribution for the gas being introduced into the fluidised or circulating bed, i.e. it will spread the entry of gas into the fluidised or circulating bed. The electrically conducting mesh may be made from any suitable material but is preferably made from stainless steel, copper or the like.

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[0041] In many means for forming excited and/or unstable gas species suitable for use in the method of the present invention there may be substantially no charged species introduced into the downstream region or in the visible plume projecting outwardly from the slit in the electrode configuration. Hence, substantially all charged species formed during  
10 excitation of the gas remain between the electrodes which generate a plasma and/or where dielectric barrier discharge and/or corona discharge occurs. The visible plume is substantially the effect of high energy neutral particles such as metastable atoms and/or molecules giving off energy when returning to their ground state. However, other systems may contain charged particles within the visible plume. Preferably the electrically conducting mesh has a voltage  
15 applied to it such that it will attract or repel all positively or negatively charged molecules present in the plume and thereby prevent said charged molecules from entering the downstream region in the fluidised or circulating bed.

[0042] In the case where a fluidised or rotating bed is utilised non-functionalised  
20 powder and/or functionalising precursor may be introduced into the bed at any appropriate position but is preferably introduced directly into the downstream region(s) of excited and/or unstable gas.

[0043] Alternative reactors which may be utilised for the method in accordance with  
25 the present invention include, for example rotating drums, rotary kilns, jet mixers, flat bed reactors (FBR) with recycle/ageing loops, static mixing reactors, sonic mixing reactors, vibrating beds, conveyor belts, tumblers alone or in any suitable combination.

[0044] Preferably ageing and/or recycling loops may be provided. These may be  
30 particularly useful when a predetermined particle size is required with respect to the functionalised powdered product.

[0045] Functionalised particles resulting from the method in accordance with the present invention may be collected by any suitable means for example they may be collected by electrostatic precipitators, filters, cyclones, scrubbers and/or electrophoresis and the like. Other options for collecting the resulting product include a statically electric charged porous plate or a vibrating sieve placed in line with the exit of the powdered particles from the plasma region to collect the resulting powdered particles.

[0046] The powdered substrate interacts with the excited and/or unstable gas and functionalised precursors in the downstream region. The excited and/or unstable gas comprises high energy non-charged particles such as gas molecules in excited states, metastable atoms and/or compounds, molecular fragments and/or radicals.

[0047] The method in accordance with the present invention is particularly suited for functionalising powdered substrates which are sensitive to other functionalising type processes and are particularly useful for functionalising powdered substrates which are sensitive to, for example, heat, temperature and UV light.

[0048] The powdered substrates to be functionalised may comprise any suitable material, for example metals, metal oxides, silica and silicates, carbon, organic powdered substrates, including polymeric, dyestuffs, fragrances, flavourings, pharmaceutical powdered substrates such as penicillins and antibiotics as well as biologically active compounds for example proteins, including enzymes and other protein based materials. The powdered substrate may also comprise biochemical compounds such as amino acids and/or their derivatives, grafted or covalently bonded biochemical compounds such as proteins, enzymes and DNA, silicone resins, mineral fillers such as for example carbon black, clays,  $\text{CaCO}_3$ , talc, silica, mica conductive fillers,  $\text{TiO}_2$  nanoparticles, metal oxides such as  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$ ,  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{PbO}$ ,  $\text{ZnO}$ , or,  $\text{CaO}$ ,  $\text{Pb}_3\text{O}_4$  and  $\text{CuO}$  and mixed oxides, graphite, phosphorus particles, pigments and the like; metalloid oxides, mixed oxide, organometallic oxides, organometaloid oxides, organomixed oxide resins and/or an organic resin, sodium carbonate potassium nitrate, silicon metal particles, silicone rubber crumb, organic rubber crumb such as EPDM and Polypropylene

[0049] It is to be understood that the functionalising precursor may be used to functionalise any appropriate powdered substrate and/or chemically modify an existing powdered substrate surface. The type of functionalisation formed on the powdered substrate surface is determined by the functionalising precursor and gas used to form excited and/or unstable species in accordance with the present invention.

[0050] Organometalloid liquid functionalised precursors may contain any suitable groups, in addition to the functional group of interest, which may react in the excited and/or unstable gas into which the precursor is introduced in accordance with the present invention to form the respective functionalised powdered substrate. In particular, in the case of silicon based functionalised precursors, for functionalising silicone resins, preferred groups present on the precursor include hydrogen atoms, hydroxyl groups, epoxy groups, an acryloxy group, an alkylacryloxy group, alkoxy groups and chloro groups, or alkyl or aryl groups bearing one or more of the functionalities described above. Examples of suitable metalloid alkoxides include silicon tetramethoxide and germanium tetraisopropoxide. It is to be understood that the term organometalloid liquid as used herein includes polymers of organometalloid elements and in particular in the case of silicon preferably include liquid organosilanes such as, for example diphenylsilane and dialkylsilanes, e.g. diethylsilane and functionalised silanes containing one or more of the following:- alkenyl, aryl, H, OH, amino groups, aldehyde groups alkyl halide groups, alkyne groups amido groups, carbamate groups, urethane groups, organic salts, carboxylic acid groups and their derivatives such as acid anhydride groups, organic groups containing boron atoms and phosphorus and sulphur containing groups such as mercapto and sulphido groups and grafted or covalently bonded biochemical groups such as amino acids and/or their derivatives, grafted or covalently bonded biochemical species such as proteins, enzymes and DNA.

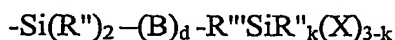
[0051] Alternatively, the precursor for silicon based products may comprise linear, branched and/or cyclic organopolysiloxanes for the formation of silica and silicates (silicone resins). The linear or branched organopolysiloxanes suitable as liquid precursors for the method of the present invention include liquids of the general formula W-A-W where A is a polydiorganosiloxane chain having siloxane units of the formula  $R''_sSiO_{4-s/2}$  in which each  $R''$  independently represents an alkyl group having from 1 to 10 carbon atoms, an alkenyl group

such as vinyl, propenyl and/or hexenyl groups; hydrogen; an aryl group such as phenyl, a halide group, an alkoxy group, a silanol group, an epoxy group, an acryloxy group, an alkylacryloxy group or a fluorinated alkyl group and generally s has a value of 2 but may in some instances be 0 or 1. Preferred materials are linear materials i.e.  $s = 2$  for all units.

- 5 Preferred materials have polydiorganosiloxane chains according to the general formula - $(R''_2SiO)_m$ - in which each  $R''$  may be the same or different and is as hereinbefore described and m has a value from about 1 to about 4000. Suitable materials have viscosities of the order of about 0.65 mPa.s to about 1,000,000 mPa.s. When high viscosity materials are used, they may be diluted in suitable solvents to allow delivery of liquid precursor in the form of a
- 10 finely dispersed atomised spray, or fine droplets, although as previously discussed, it is preferred to avoid the need for solvents if possible. Most preferably, the viscosity of the liquid precursor is in the range between about 0.65 mPa.s and 1000 mPa.s and may include mixtures of linear or branched organopolysiloxanes as hereinbefore described suitable as liquid precursors.

15

[0052] The groups W may be the same or different. The W groups may be selected, for example, from  $-Si(R'')_2X$ , or



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where B is  $-R'''-(Si(R'')_2-O)_r-Si(R'')_2-$  and

$R''$  is as aforesaid,  $R'''$  is a divalent hydrocarbon group r is zero a whole number between 1 and 6 and d is 0 or a whole number, most preferably d is 0, 1 or 2, k is 0, 1, 2 or 3, X may be the same as  $R''$  or a hydrolysable group such as an alkoxy group containing alkyl groups

25 having up to 6 carbon atoms, an epoxy group or a methacryloxy group or a halide.

- [0053] Cyclic organopolysiloxanes having the general formula  $(R''_2SiO_{2/2})_n$  wherein  $R''$  is hereinbefore described, n is from 3 to 100 but is preferably from 3 to 22, most preferably n is from 3 to 6. Liquid precursors may comprise mixtures of cyclic
- 30 organopolysiloxanes as hereinbefore defined.

[0054] The functionalised precursor may alternatively comprise suitable organic materials include carboxylates, methacrylates, acrylates, styrenes, methacrylonitriles, alkenes and dienes, for example methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, and other alkyl methacrylates, and the corresponding acrylates, including  
5 organofunctional methacrylates and acrylates, including glycidyl methacrylate, trimethoxysilyl propyl methacrylate, allyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, dialkylaminoalkyl methacrylates, and fluoroalkyl (meth)acrylates, methacrylic acid, acrylic acid, fumaric acid and esters, itaconic acid (and esters), maleic anhydride, styrene,  $\alpha$ -methylstyrene, halogenated alkenes, for example, vinyl  
10 halides, such as vinyl chlorides and vinyl fluorides, and fluorinated alkenes, for example perfluoroalkenes, acrylonitrile, methacrylonitrile, ethylene, propylene, allyl amine, vinylidene halides, butadienes, acrylamide, such as N-isopropylacrylamide, methacrylamide, epoxy compounds, for example glycidoxypropyltrimethoxysilane, glycidol, styrene oxide, butadiene monoxide, ethyleneglycol diglycidylether, glycidyl methacrylate, bisphenol A diglycidylether  
15 (and its oligomers), vinylcyclohexene oxide, conducting polymers such as pyrrole and thiophene and their derivatives, and phosphorus-containing compounds, for example dimethylallylphosphonate. Organic functionalising precursors may also include an organic compound comprising any one of the following groups alkenyl, aryl, H, -OH, amino groups, aldehyde groups alkyl halide groups, alkyne groups amido groups, carbamate groups, urethane groups, organic salts, carboxylic acid groups and their derivatives such as acid  
20 anhydride groups, organic groups containing boron atoms, phosphorus and sulphur containing groups such as mercapto and sulphido groups and grafted or covalently bonded biochemical groups such as amino acids and/or their derivatives, grafted or covalently bonded biochemical species such as proteins, enzymes and DNA.

25

[0055] Suitable inorganic coating-forming materials include metals and metal oxides, including colloidal metals. Organometallic compounds may also be suitable coating-forming materials, including metal alkoxides such as titanates, tin alkoxides, zirconates and alkoxides of germanium and erbium and mixtures thereof to make ceramic coatings on the powdered  
30 materials.

[0056] When using a functionalised precursor in liquid form, the liquid may be brought into contact with the excited and/or unstable gas by any suitable means. In a preferred embodiment the liquid precursor is preferably introduced into excited and/or unstable gas by way of a liquid spray through an atomiser or nebuliser (hereinafter referred to as an atomiser) as described in the applicants co-pending application WO 02/28548. This provides the invention with a major advantage over the prior art in that the liquid precursor may be introduced into the excited and/or unstable gas in the absence of a carrier gas, i.e. a liquid precursor can be introduced directly into the excited and/or unstable gas by, for example, direct injection directly into the excited and/or unstable gas. Hence, the inventors avoid the need for the essential features of US 20020192138 that as discussed above requires both very high working temperatures and the need for the salts to be in a vaporous form.

[0057] Any suitable atomiser may be utilised for the atomisation and introduction of said liquid precursor, examples include the use of an ultrasonic nozzle or pneumatic nebulisers and nozzles. The atomiser preferably produces a liquid precursor drop size of from 10 nm to 100µm, more preferably from 1µm to 50µm. Suitable atomisers for use in the method in accordance with the present invention are ultrasonic nozzles from Sono-Tek Corporation, Milton, New York, USA or Lechler GmbH of Metzingen Germany and Pneumatic nozzles or intersurgical chambers from Clement Clarke International.

[0058] The apparatus which may be utilised in the method in accordance with the present invention may include a plurality of atomisers.

[0059] The functionalised powdered substrate may be post treated with any appropriate treatment, for example it may undergo a plasma treatment. Post treatment is likely to involve the application of coatings or modification of the functionality. For example, a functionalised substrate may be post treated in a range of plasma conditions, to e.g. oxidise or reduce the initial functionalising group attached to the substrate.

[0060] Powdered substrates coated by the method of the present invention may have various utilities. For example, a silica based coating may give encapsulation through enhanced barrier (oxygen and/or moisture) properties and controlled release properties to an

organic particle such as a fragrance, flavour, pharmaceutical or dyestuff. Improved compatibility could be achieved for metal or metal oxide powders used as reinforcing or property modifying fillers in rubbers and plastics. Improved compatibility may also be utilised for dispersions such as dyestuffs/pigments, antioxidants and UV stabilisers in polymer materials and also formulated products such as paints and cosmetics. Powder processing may be improved by enhancing characteristics such as flow, compatibility and electrostatic properties. Specific functionalities may be added to catalysts and catalyst support to enhance or control reactivity. Also surface and pore properties of powders used as separation media or as support for separation media may be controlled.

[0061] In one embodiment of the invention a statically electric charged porous plate or a vibrating sieve may be placed in line with the exit of the powdered substrate from the plasma region to collect the resulting powdered substrate.

[0062] There are a wide variety of uses for powders functionalised by the method of the present invention. These include:-

i) Functionalised crumb silicone and/or organic rubber (eg, Natural rubber, EPDM SBR and NBR), Polypropylene and Thermosets

i.e. powdered rubber recycled from e.g. tyres made from particulates of varying sizes ranging from 200 to 1500  $\mu\text{m}$  for reuse in organic or silicone based composites.

Functionalised Nanoparticles for application onto flexible substrates for sensors, eg biosensor applications and for photonics applications e.g. luminescence and photonic crystals.

Functionalised organofunctional silicone resins for incorporation of said resins in a wide variety of compositions. Applications include, for example, adding flexibility and abrasion resistance in protective coatings used in the automotive industry.

Functionalised conductive fillers for surface treatment of microprocessors mixed in silicone elastomers to protect filler surfaces from oxidation at high temperature and humidity level to prevent lower electrical conductivity.

[0063] Functionalised nanodispersions of  $\text{TiO}_2$  in organopolysiloxane polymers with higher Refractive Indices for optical uses like antireflective coatings for display devices,

intra-ocular and optical lenses, optical amplifying fibres, high Refractive index adhesives, photonic crystals or for cosmetic application e.g. hair care composition with enhance shine.

[0064] Tough resin adhesion to carbon, graphite graphite fibres and more broadly  
5 glass quartz and stainless steel is very difficult. The targeted markets for use in the flexible electronics, solid state lighting, thin film batteries and photovoltaic cells.

[0065] Surface treatment of pigments as fillers e.g.  $\text{TiO}_2$ , Carbon black,  $\text{SiO}_2$ ,  $\text{CaCO}_3$ ,  
10  $\text{Al}_2\text{O}_3$ . in aqueous and organic media while maintaining the rheology, colour intensity, and hiding power properties e.g. a colour stabilization and enhancement treatment, for use in automotive, coating, tyre and wood industries, low cost filler applications.

[0066] 3-Dimensional deposition in aqueous phase to improve the deposition yield of  
15 silicones either or both in the washing and rinsing cycles for fabric care application.

[0067] Encapsulation/functionalisation of actives specifically vitamins, sunscreens  
and fragrances for e.g. their delivery by controlled release, Surface activation to improve  
deposition of active ingredients onto specific substrates and improved targeting to delivery  
active ingredients to specific sites of action. Use in Physical or chemical stabilization of  
20 active ingredients that are unstable to oxygen, heat and / or light.

[0068] There is a need for an encapsulation process that is low cost, gives efficient  
protection and controlled delivery. The encapsulants must be water soluble or compatible to  
allow formulation and delivery of actives such as biomolecules: vitamins A, C, D, E;  
25 phospholipids, alkylpoly glucosides, betaine, sodium lauryl sulfate, fragrance, drugs, UV blockers, incompatible components like organic oils, dyes, which need protection for several months for stability against oxygen, water, and agglomeration. The encapsulants are required for 4 distinct applications, encapsulated sunscreens, functionalized sunscreens, encapsulated vitamins A, C, E and controlled hypoallergenic fragrance release

30 [0069] Formulations of solid particles. The formulation and compatibilisation of pigments for healthcare, fabric care, skin care, personal care and hair care (conditioners) is



limited due to the surface chemistry and size of the particles. Nano-particles are not used today due to their tendency to aggregate, their high surface reactivity and for compatibility issues. There is a need for homogeneous treatment of pigment particles ( $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{ZnO}$ , Clay, mica) for hydrophobic, lipophobic, hydrophilic properties as well as for electrical properties modification for better formulation compatibility.

[0070] Plasma generation of pigments can lead to nanoparticles for which the surface can be further chemically activated by a simple plasma process. In-situ and direct formulation will allow small particles to be incorporated in media of choice. Furthermore, suitable pairs of pigments and liquid polymer or surfactants will allow stability in-situ. Small size of particles will provide various benefits such as transparency or scattering to light, different feel, high chemical reactivity, and long-term stability.

[0071] Encapsulation and functionalisation of micro and nano-particles should also be of interest for the coating industry. Improving compatibility of silicones with organic actives, oils and polymers. Functionalisation of filter media with various ligands, chemical groups, and enzymes be for selective separation, filtration, solid phase extraction. Surface activation & functionalisation of mineral fillers (carbon black, clays,  $\text{CaCO}_3$ , talc, silica)

- Conductive fillers treatment for microprocessors
- $\text{TiO}_2$  nanodispersion in organopolysiloxane polymers
- $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Fe}_2\text{O}_3$  and mixed oxides layers for high Refractive index
- $\text{SiO}_2$  for low dielectric constant
- ITO films
- Multilayered coatings with variable properties• Solventless resin or in customers desirable solvent
- Tough resin adhesion to graphite
- Phosphorus particles encapsulation for Solid state lighting and LED
- Activation/passivation of particles (metals, plastics)
- Encapsulation of actives (sunscreen, dyes, vitamins, fragrance)
- Compatibility of Chemicals

- Compatibility & formulation of solid particles (personal care)
- Surface treatment of pigments/fillers
- Pigment treatment for plastic adhesion
- Separation membranes
- 5 • PDMS 3D deposition on fabric in aqueous phase (washing/rinsing)
- PDMS 3D deposition on fabric (tumble dryer)
- Charging particles (+/-)
- Powder coating
- Graphite surface activation

10

[0072] The present invention will now be described further on the basis of the following examples and drawings in which :-

15

Fig. 1 shows a schematic view of a means for generating excited and/or unstable gas species according to the invention;

Fig. 2 schematically shows a fluidised bed adapted to fit the means as shown in Fig. 1

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Fig.3 is a detailed schematic drawing of a fluidised bed in accordance with the present invention.

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[0073] Referring to Fig. 1, Fig 1 shows a means for generating excited and/or unstable gas species 1, having a inlet 2 to a gas homogenisation chamber 3, an inlet 4 for a gas to enter the electrode configuration 15. The electrode configuration 15 comprises an outer electrode 5 an inner electrode 6 and a layer of dielectric material on the inner electrode 7. The gap 9 between dielectric 7 and outer electrode 5 is adapted to receive and channel all gas entering inlet 4 from chamber 3 to an excited and or unstable gas species outlet slit 10. Gap 9 is tubular and preferably has an axial length of up to 1 metre but is typically less than 50 cm long. The width of gap 9 is up to 100mm but is preferably less than 10mm. Slit 10 extends  
30 over the full axial length of the system.

[0074] Electrodes 5 and 6 are connected to a high voltage and high frequency electrical generator 8 operating at a frequency of greater than 15kHz and delivering a power of in the order of 10kW.

5 [0075] In use a gas to be rendered excited and/or unstable is introduced into homogenisation chamber 3 through inlet 2 and subsequently into the electrode configuration 15. The gas is rendered excited and or unstable whilst in gap 9 wherein it forms a plasma or is subjected to dielectric barrier discharge or corona discharge. The charged species formed within gap 9 remain in gap 9, but the gas comprising excited and/or unstable species leaves  
10 configuration 15 through outlet 10 and forms a downstream region 11 in which region it interacts with precursor to form the powder and/or discrete gel particles in accordance with the present invention. A plume 40 is visible to the naked eye and is believed to be the result of previously excited and/or unstable species giving off energy when returning to their ground state after having existed in said excited state for a period of time in the in the downstream  
15 region.

[0076] Fig.2 shows an embodiment of the invention where a means 1 in accordance with the invention is adapted for use in a fluidised bed 20, such that gas enters entrance 2 and subsequent to excitation of the type described in relation to Fig. 1 above leaves the  
20 configuration through exit slit 10 and enters the fluidised bed 20. The flow rate of the gas passing through means electrode configuration 15 is such that it also acts as the fluidising gas in the fluidised bed 20. The downstream region is identified 11 and the plume is seen at 40 along the exit slit 10.

25 [0077] Fig. 3 is a more detailed schematic drawing of a fluidised bed in accordance with the method of the present invention including a means of forming excited and/or unstable gas species 1a as described in conjunction with figs. 1 and 2. Alternative and/or additional sites for means of forming excited and/or unstable gas species are identified by numerals 1b and 1c. A means for introducing a liquid precursor 50a is provided at the top of  
30 the fluidised bed and an alternative and/or additional means for same is indicated at 50b. Preferably such means 50a and 50b introduce liquid precursor in the form of a liquid spray through an atomiser or nebuliser of the type described in the applicants co-pending application

WO 02/28548. A slide valve 56 is provided immediately above the means of forming excited and/or unstable gas species 1a, this is intended as a means of preventing powder and precursor from entering electrode configuration 15 (Fig. 1) once the flow of gas through means 1 has been switched. This valve may be replaced by the mesh as described previously  
5 where appropriate. Waste gases may be removed from the fluidised bed 20 via 52 and are seen to be removable using a pneumatic conveying apparatus at the base of the fluidised bed 54.

## EXAMPLE 1

[0078] Rice hull ash was fed into a 8 L reaction chamber on which was attached the  
5 post plasma source. A 1:1.2 mixture of 1,3,5,7-tetramethylcyclotetrasiloxane in 1,3,5,7,9-  
pentamethylcyclopentasiloxane was sprayed via a pneumatic nebulisation nozzle into the  
post plasma reactor and within the post discharge atmospheric plasma phase and thus over 35  
min. The reactive gas mixture was 250 l/min of nitrogen (N<sub>2</sub>). The power of the post  
discharge atmospheric plasma is 2,200 W. The resulting treated rice hull ash was recovered  
10 and further analysed. The composition of the resulting treated rice hull ash was determined  
by <sup>29</sup>Si MAS NMR spectroscopy. The powder was functionalised with an organosilicon  
material of D<sup>H</sup>TQ composition. NMR result also indicated covalent reaction between the  
surface of the rice hull ash substrate with organosilicone material. It was found that the  
treated rice hull ash was floating on water whereas the untreated rice hull ash substrate sank.

15

## EXAMPLE 2

[0079] A fluidised bed reactor was constructed with a 200mm square section in 4mm thick  
polycarbonate. The reactor consists of a straight section of height approx 1m together with an  
expanded head of square section 300mm, also of height approx 1m. The base tapers to a  
20 rectangular slit of cross section approx 150mm x 30mm. To avoid material build-up on  
surfaces, vertical angles are limited to no less than 20 degrees from vertical. (ie max cone  
angle 40 degrees at the base). The polycarbonate was readily fused together by means of a  
hot air gun.

25 [0080] The rectangular slit was then fitted with a 4mm polycarbonate flange adapted to be  
suitable with respect to the dimensions of plasma generating device utilised. The  
atmospheric pressure glow discharge plasma generating device was then attached to the base  
of the reactor together with a gasket for sealing. A slide valve was also incorporated into the  
assembly to enable closure of the base of the reactor above the plasma device and to enable  
30 shutdown without contamination of the plasma device.

[0081] Liquids are sprayed into the unit with one or more nebulizing devices capable of generating liquid droplets at about 1-10 micron size (eg Cirrus™ Nebulizer code 1501 sold by Intersurgical). Depending on the liquid in question the carrier gas can be air or an inert gas (e.g. nitrogen). Typical entry point for the nebulized liquid stream is at the start of the square section or approx 200mm away from the plasma head. In use the droplets enter the region inhabited by excited species generated by the plasma generating assembly and the powdered substrate and the powdered substrate is functionalised due to their interactions.

[0082] Solids recovery was achieved with an external cyclone designed for inlet velocities of approximately 50 ft per second. Solids were returned by suction with a venturi nozzle operating at about 20 litres per minute compressed air (or inert gas) enabling solids return to the reactor from the base of the cyclone. The venturi nozzle used had an orifice diameter of 0.9 mm and an air/gas supply pressure of 6bar gage.

#### EXAMPLE 3

[0083] 200 g to 2 kg of rice hull ash (RHA) was fed into the fluidised bed reactor described in Example 1. The substrate was fluidised in contact with the excited species generated by the plasma assembly (hereafter referred to as "atmospheric plasma post-discharge" for a period of 30 minutes in the presence of an oxidatising gas, resulting in an oxidative plasma post-treatment of the substrate. The reactive gas mixture was 250 l/min of air. The power delivered to the plasma assembly was 1,800 W. RHA treated in accordance with the present invention was sampled over time for NMR characterization and wettability analysis. The wettability test comprising the step of deposition of a water droplet revealed that the oxidative plasma post-discharge treated RHA was more hydrophilic than for the raw powder. <sup>29</sup>Si NMR confirmed the formation of reactive hydroxysilyl functionality. The O<sub>1.5</sub>SiOH/SiO<sub>2</sub> ratio was increased by up to 35% over time by plasma post-discharge treatment also call "surface activation".

#### EXAMPLE 4:

[0084] 200g of RHA were fed into the fluidised bed reactor described in Example 1. The substrate was fluidised in contact with the atmospheric plasma post-discharge for a period of

30 min. The reactive gas mixture was 250 L/min of air. The power delivered to the plasma source of the atmospheric plasma post discharge was 1,800 W.

[0085] After plasma post-discharge surface activation, the plasma source was switched off and 20g of n-octyltriethoxysilane were sprayed *via* two pneumatic nebulisation nozzles into the reactor and thus over 35 min. The treated substrate was sampled for further NMR and wettability analysis. Wettability test by deposition of a water droplet revealed that the treated RHA was partially hydrophobic.  $^{29}\text{Si}$  NMR and  $^{13}\text{C}$  NMR confirmed the functionalisation of the rice hull ash substrate with n-octylsilyl groups.

[0086] Oxidative plasma post-treatment was applied to the n-octylsilyl-treated RHA for a period of 3 min. under the same process conditions than described earlier (250 L/min. of air, 1,800 W). The final powder was recovered and analysed by NMR and video contact angle(VCA). A sessile drop of water (1  $\mu\text{L}$ ) deposited on a packed bed of RHA displayed a contact angle of  $146^\circ$ , showing very high hydrophobicity property of the powder. NMR confirmed the retention of n-octyl functionality and a higher condensation degree compared to before post-plasma treatment.

#### EXAMPLE 5:

[0087] 200g of RHA were fed into the fluidised bed reactor described in Example 1. The substrate was fluidised in contact with 250 L/min. of  $\text{N}_2$  gas without plasma for a period of 15 min. 20g of a 1,3,5,7-tetramethylcyclotetrasiloxane, 1,3,5,7,9-pentamethylcyclopentasiloxane and 1,3,5,7,9,11-hexamethylcyclohexasiloxane mixture were sprayed into the reactor *via* a pneumatic nebulisation nozzle and thus over 35 min. The treated substrate was sampled for further NMR and solvents wettability analysis. Wettability test by deposition of a water droplet revealed that the treated RHA was hydrophobic.  $^{29}\text{Si}$  NMR confirmed the partial functionalisation of the RHA substrate with  $\text{SiH}$  ( $\text{D}^{\text{H}}$  sub-units) and  $\text{SiMe}$  ( $\text{D}^{\text{H}}$  and  $\text{T}^{\text{Me}}$  sub-units) groups. Dispersing the powder and washing with toluene revealed that up to 50 mol % of the  $\text{D}^{\text{H}}$  species are not covalently bonded to the RHA substrate.

[0088] Oxidative plasma post-treatment was applied to the methylhydrogensilyl-treated RHA for a period of 10 and 40 min. under the same process conditions than described earlier

(250 L/min. of air, 1,800 W). Powders were sampled over time and analysed by NMR and wettability test. The hydrophobic powder upon post-plasma treatment became progressively fully wettable with water. NMR confirmed the degradation of the D<sup>H</sup> sub-units and conversion under oxidative conditions to O<sub>1.0</sub>SiMeOH and O<sub>1.5</sub>SiOH for a higher degree of reactivity *via* oxidative plasma post-discharge surface activation. Thermogravimetric analysis (TGA) ran in air atmosphere showed same degree of weight loss upon heating from 120 to 600°C, indicating that the main polysiloxane structure remains on the surface of the RHA in support of the NMR analysis with only the substitution of hydrogen and/or methyl groups with hydroxyl groups.

#### EXAMPLE 6:

[0089] 200g of RHA were fed into the fluidised bed reactor described in Example 1. The substrate was fluidised in contact with the atmospheric plasma post-discharge for a period of 30 minutes. The reactive gas mixture was 250 L/min of air. The power delivered to the plasma source of the atmospheric plasma post discharge was 1,800 W.

[0090] After plasma post-discharge surface activation, the plasma source was switched off and 20 g of a mixture of 1,3,5,7-tetramethylcyclotetrasiloxane, 1,3,5,7,9-pentamethylcyclopentasiloxane and 1,3,5,7,9,11-hexamethylcyclohexasiloxane were sprayed into the reactor *via* a pneumatic nebulisation nozzle and thus over 35 min. The treated substrate was sampled for analyses. Wettability by deposition of a water droplet revealed that the treated RHA was hydrophobic. The sample was rinsed with CH<sub>2</sub>Cl<sub>2</sub>/toluene and further dispersed and washed with toluene before analysis by NMR and VCA. The hydrophobic powder upon washing treatment had a contact angle of a 1 µL water droplet of 125°. <sup>29</sup>Si NMR confirmed the covalent functionalisation of RHA with SiH (D<sup>H</sup> sub-units) to a much larger extend than for RHA not activated with plasma (Example 4), and SiMe (D<sup>H</sup> and T<sup>Me</sup> sub-units) groups. TGA confirmed the attachment of the polysiloxane molecules on the surface of RHA.

[0091] Oxidative plasma post-treatment was applied to the hydrogenmethylsilyl-treated RHA for a period of 30 min. under the same process conditions than described earlier (250 L/min. of air, 1,800 W). Powders were sampled and analysed by NMR and wettability test. The powder upon oxidative post-plasma treatment became slightly hydrophilic. NMR



confirmed the degradation of most of the D<sup>H</sup> sub-units and conversion under oxidative conditions to reactive O<sub>1,0</sub>SiMeOH and to a larger extends O<sub>1,5</sub>SiOH functional species.

[0092] The plasma source was switched off and 20g of 3-aminopropyltriethoxysilane were sprayed *via* a pneumatic nebulisation nozzles into the reactor and thus over 35 min. The partially hydrophilic powder was rinsed with CH<sub>2</sub>Cl<sub>2</sub>/toluene and further dispersed and washed with toluene before further analysis. <sup>29</sup>Si NMR, TGA and DRIFT fourier Transform Infra-red (FTIR) confirmed the functionalisation of the rice hull ash substrate with methyl and 3-aminopropylsilyl groups.

#### EXAMPLE 7:

[0093] 200g of TiO<sub>2</sub> powder (anatase) were fed into the fluidised bed reactor described in Example 1. The substrate was fluidised in contact with the atmospheric plasma post-discharge for a period of 30 min. The reactive gas mixture was 250 L/min of air. The power delivered to the plasma source of the atmospheric plasma post discharge was 1,800 W. Plasma post-discharge treated TiO<sub>2</sub> was sampled for wettability analysis. Wettability test by deposition of a water droplet revealed that the treated titania was even more hydrophilic than for the raw powder.

[0094] After plasma post-discharge surface activation, the plasma source was switched off and 20g of a 1,3,5,7-tetramethylcyclotetrasiloxane, 1,3,5,7,9-pentamethylcyclopentasiloxane and 1,3,5,7,9,11-hexamethylcyclohexasiloxane mixture were sprayed into the reactor *via* two pneumatic nebulisation nozzles and thus over 20 min. The treated substrate was sampled for further analysis. Wettability test by deposition of a water droplet revealed that the treated titania was hydrophobic. <sup>29</sup>Si NMR, DRIFT FTIR and TGA confirmed the formation of O<sub>1,0</sub>SiMeH, O<sub>1,0</sub>SiMeOH and O<sub>1,5</sub>SiMe sub-units with retention of the surface composition upon subsequent rinsing and washing steps in CH<sub>2</sub>Cl<sub>2</sub> and toluene.

[0095] Oxidative plasma post-treatment was applied to the methylhydrogensilyl-treated titania for 5 min. under the same process conditions than described earlier (250 L/min. of air, 1,800 W). Powders were sampled and analysed. Wettability test by deposition of a water droplet revealed that the treated titania was hydrophilic again. <sup>29</sup>Si NMR, DRIFT FTIR and

TGA confirmed the retention of the  $O_{1.5}SiMe$  sub-units and the partial conversion of  $O_{1.0}SiMeH$  sub-units into  $O_{1.0}SiMeOH$  and  $O_{1.5}SiMe$  sub-units.

[0096] The plasma source was switched off again and 20g of n-octyltriethoxysilane were sprayed *via* two pneumatic nebulisation nozzles into the reactor over 30 min. The hydrophilic powder became superhydrophobic upon treatment with a contact angle of a 1  $\mu$ L water droplet of  $150^\circ$ . TGA,  $^{29}Si$  NMR,  $^{13}C$  NMR and DRIFT FTIR confirmed the functionalisation of titania with  $SiH$  ( $D^H$  sub-unit),  $SiMe$  ( $D^H$  and  $T^{Me}$  sub-units) and  $SiOctyl$  ( $T^{Octyl}$  sub-unit) groups.

#### EXAMPLE 8:

[0097] 200g of  $TiO_2$  powder (anatase) were fed into the fluidised bed reactor described in Example 1. The substrate was fluidised in contact with 250 L/min. of air without plasma for 16 min. 20g of a 1,3,5,7-tetramethylcyclotetrasiloxane, 1,3,5,7,9-pentamethylcyclopentasiloxane and 1,3,5,7,9,11-hexamethylcyclohexasiloxane mixture were sprayed into the reactor *via* two pneumatic nebulisation nozzles and thus over 20 min. The treated substrate was sampled for wettability analysis. Wettability test by deposition of a water droplet revealed that the treated titania was still hydrophilic as for the raw material, revealing that functionalisation did not occur or was minimal.

[0098] Oxidative plasma post-discharge treatment was applied to the powder for 12 min. under the same process conditions than described earlier (250 L/min. of air, 1,800 W). The plasma source was switched off and 14g of a 1,3,5,7-tetramethylcyclotetrasiloxane, 1,3,5,7,9-pentamethylcyclopentasiloxane and 1,3,5,7,9,11-hexamethylcyclohexasiloxane mixture was sprayed into the reactor *via* two pneumatic nebulisation nozzles and thus over 11 min. The treated substrate was sampled for wettability analysis. Wettability test by deposition of a water droplet revealed that the treated titania was now hydrophobic, revealing that plasma-assisted functionalisation did effectively occur.

#### EXAMPLE 9:

[0099] 6.6g of  $TiO_2$  powder (anatase) were dispersed into 6.6g of a 1,3,5,7-tetramethylcyclotetrasiloxane, 1,3,5,7,9-pentamethylcyclopentasiloxane and 1,3,5,7,9,11-

hexamethylcyclotrisiloxane mixture in 40 ml of toluene in a glass reaction vessel. The mixture was stirred 5 hours at room temperature. The solid was filtrated and rinsed with  $\text{CH}_2\text{Cl}_2$  and toluene. The solid was re-dispersed into 50 ml of toluene and stirred overnight. The powder was filtrated, rinsed and dried prior to NMR, DRIFT FTIR and wettability analysis. Wettability test by deposition of a water droplet revealed that the treated titania was still hydrophilic as for the raw titania. No silicon containing functionalities were observed by  $^{29}\text{Si}$  NMR.

#### EXAMPLE 10:

10 [0100] 200g of  $\text{TiO}_2$  powder (anatase) were fed into the fluidised bed reactor described in Example 1. The substrate was fluidised in contact with the atmospheric plasma post-discharge for a period of 10 min. The reactive gas mixture was 250 l/min of air. The power delivered to the plasma source of the atmospheric plasma post discharge was 1,800 W.

15 [0101] After plasma post-discharge surface activation, the plasma source was switched off and 20g of n-octyltriethoxysilane were sprayed into the reactor *via* two pneumatic nebulisation nozzles and thus over 25 min. The treated substrate was sampled for further analysis. The hydrophilic powder became super hydrophobic upon treatment with a contact angle of a 1  $\mu\text{L}$  water droplet of  $150^\circ$ .  $^{29}\text{Si}$  NMR,  $^{13}\text{C}$  NMR, and TGA confirmed the functionalisation of titania with  $\text{SiOctyl}$  ( $\text{T}^{\text{Octyl}}$  sub-unit) groups. TGA under air atmosphere  
20 showed a weight loss attributed to the oxidation of hydrocarbons.

[0102] Oxidative plasma post-discharge treatment was applied to the octylsilyl-functional titania powder for 1 min. under the same process conditions than described earlier (250  
25 L/min. of air, 1,800 W). The final powder was recovered and analysed by NMR and VCA. The powder was still superhydrophobic upon post-treatment with a contact angle of a 1  $\mu\text{L}$  water droplet of  $152^\circ$ . NMR confirmed the retention of the n-octyl functionality and a higher condensation degree compared to before post-plasma treatment.

### CLAIMS

1. A method of functionalising a powdered substrate, which method comprises the following steps:-
  - i) passing a gas into a means for forming excited and/or unstable gas species;
  - ii) treating said gas such that upon leaving said means the gas comprises excited and/or unstable gas species which are substantially free of electric charge; at a temperature below 400°C.
  - iii) treating the powdered substrate with said excited and/or unstable gas species and a functionalising precursor both of which have not been subjected to steps (i) and (ii); in a downstream region external to the means for forming excited and/or unstable gas, wherein said functionalising precursor is introduced simultaneously with or subsequent to introduction of the powdered substrate;
  - iv) collecting resulting functionalised substrate.
2. A method in accordance with claim 1 wherein the means to generate excited and/or unstable gas species is an electrical discharge apparatus.
3. A method in accordance with claim 1 or 2 wherein the powdered substrate and/or functionalised precursor is/are treated by the excited and/or unstable gas species in a container.
4. A method in accordance with claim 3 wherein the container is a fluidised bed and/or circulating bed reactor.
5. A method in accordance with claim 4 wherein the gas comprising excited and/or unstable gas species is utilised as the gas in the fluidised or circulating bed for suspending powders, and/or droplets of liquid.

6. A method in accordance with any preceding claim wherein the liquid and/or gas functionalising agent is in the form of a liquid compound, a solution of a high viscosity liquid or solid compound in either a liquid carrier or a liquid co-reactive and/or a molten solid.
7. A method in accordance with claim 6 wherein the liquid functionalising precursor comes into contact with the powder substrate in or not in the presence of the excited and/or unstable gas species.
8. A method in accordance with any preceding claim wherein the functionalised precursor is introduced in the form of an atomised liquid.
9. A method in accordance with claim 3, 4 or 5 wherein the atomised liquid is introduced into the container at any position by direct injection.
10. A method in accordance with any one of claims 1 to 5 wherein the liquid and/or gas functionalising agent is an organometallic compound of titanium, zirconium, iron, aluminium, indium and tin or mixtures containing one or more thereof.
11. A method in accordance with any one of claims 1 to 5 wherein the liquid and/or gas functionalising agent is an organometalloid compound of germanium or silicon.
12. A method in accordance with claim 10 wherein the organometalloid compound is selected from an organosilane and an inorganic silane where the inorganic groups are selected from halogeno, hydrogeno, or hydroxyl groups, and mixtures thereof.
13. A method in accordance with claim 11 wherein the organosilane is a functionalised silane containing one or more of the following organic groups

bearing functionalities such as:- alkenyl, aryl, H, OH, amino groups, aldehyde groups alkyl halide groups, alkyne groups amido groups, carbamate groups, urethane groups, organic salts, carboxylic acid groups and their derivatives such as acid anhydride groups, organic groups containing boron atoms, or phosphorus, or sulphur containing groups such as mercapto, or sulphido groups or grafted or covalently bonded biochemical groups such as amino acids and/or their derivatives, grafted or covalently bonded biochemical species such as proteins, enzymes and DNA.

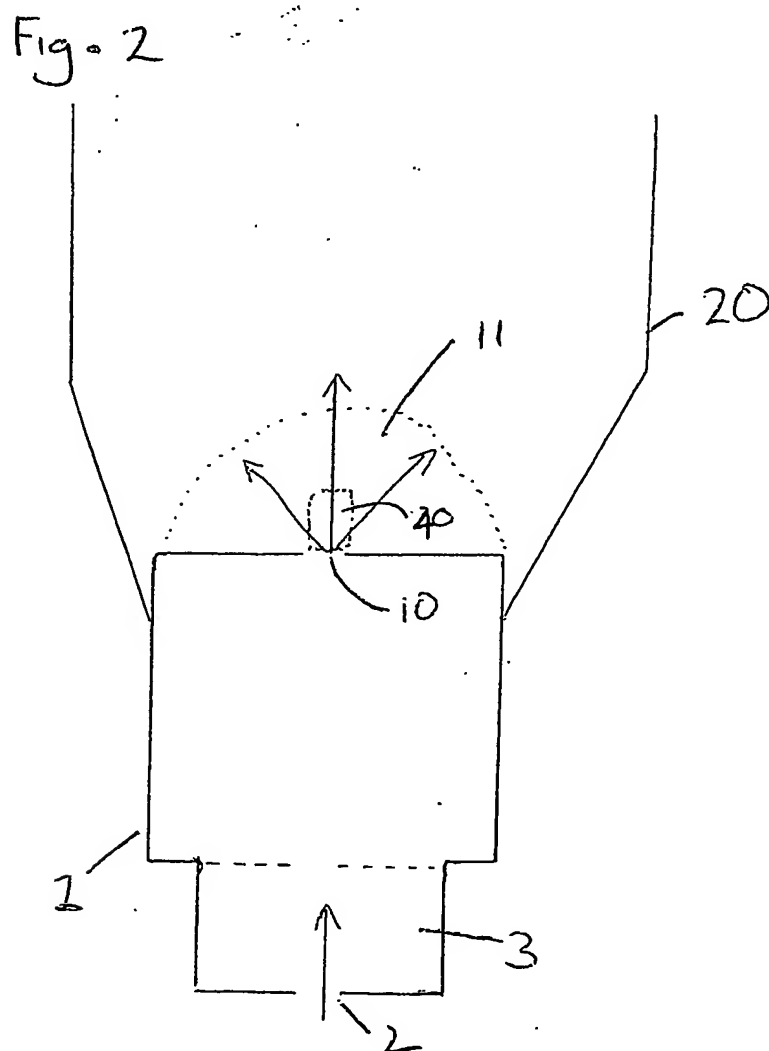
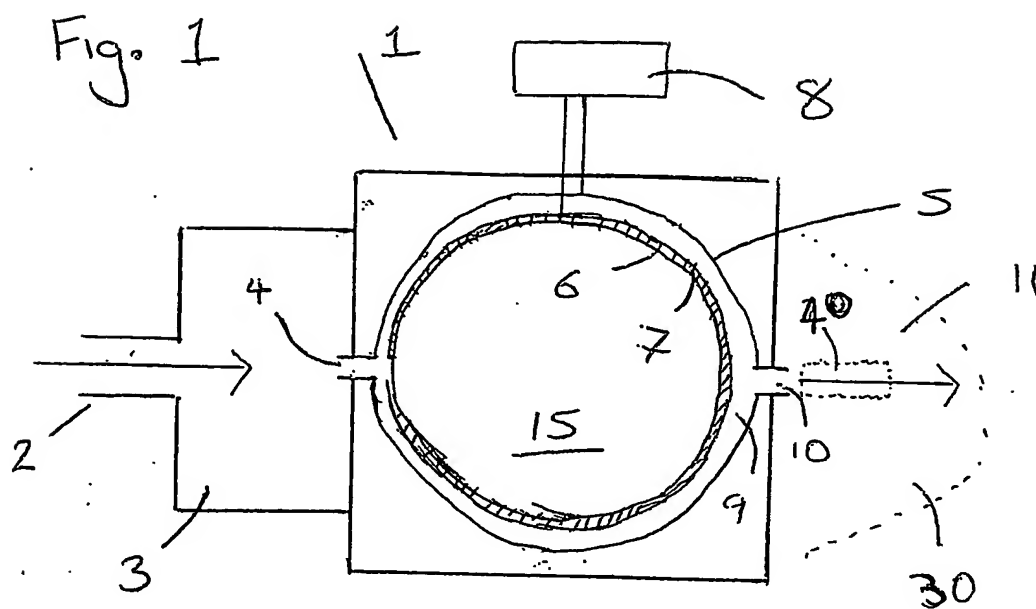
14. A method in accordance with claim 10 wherein the organometalloid compound is an organopolysiloxane having a viscosity of from 0.65 to 1000 mPa.s.
15. A method in accordance with any one of claims 1 to 5 wherein the functionalising precursor is an organic compound.
16. A method in accordance with any one of claims 1 to 14 wherein the powder substrate is selected from one or more of a compound selected from the group of a metallic oxide, a metalloid oxide, a mixed oxide, an organometallic oxide, an organometalloid oxide, an organomixed oxide resin, and/or an organic resin.
17. A method in accordance with any one of claims 1 to 14 wherein the powdered substrate is selected from one or more of the following:-  
metals, metal oxides, silica and silicates, carbon, carbon nanotubes, carbon and silicon nanostructures, organic powdered substrates, including polymeric, dyestuffs, fragrances, flavourings, pharmaceutical powdered substrates such as penicillins and antibiotics as well as biologically active compounds for example proteins, including grafted or covalently bonded biochemical groups such as amino acids and/or their derivatives, grafted or covalently bonded biochemical species such as proteins, enzymes and DNA and other protein based materials, silicone resins, mineral fillers such as for example carbon black, clays,  $\text{CaCO}_3$ , talc, silica, biogenic silica, mica conductive fillers,  $\text{TiO}_2$

nanoparticles, metal oxides such as  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$ ,  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{PbO}$ ,  $\text{ZnO}$ , or,  $\text{CaO}$ ,  $\text{Pb}_3\text{O}_4$  and  $\text{CuO}$  and mixed oxides, graphite, phosphorus particles, organic and inorganic pigments and the like; metalloid oxides, mixed oxide, organometallic oxides, organometalloid oxides, organomixed oxide resins and/or an organic resin, sodium carbonate potassium nitrate, silicon metal particles, silicone rubber crumb, organic rubber crumb such as EPDM and polypropylene, wood dust and/or plastics.

18. A powder substrate according to claim 15 that has been functionalised according to functionalities described in claims 9,10,11,12.
19. A powder in accordance with claim 15 having a particle size of from 1nm to 20 mm.
20. An apparatus for making functionalised particles by the method of claims 1 to 14 or 16 comprising a means for generating an excited and/or unstable gas species, a means adapted to introduce the powder substrate, and a means to introduce a gaseous and/or liquid precursor into said excited and unstable gas species in a downstream region external to the means forming excited and/or unstable gas, and a means for collecting resulting functionalised powder.
21. An apparatus in accordance with claim 19 wherein said apparatus forms a part of a fluidised or circulating bed.
22. An apparatus in accordance with claim 19 or 20 wherein the means adapted to introduce a gaseous and/or liquid precursor is an atomiser.
23. An apparatus in accordance with any one of claims 19, 20 or 21 wherein means for generating an excited and/or unstable gas species is an electrical discharge assembly.

24. Use of functionalised powder particles in accordance with any of claims 15 to 18 in optoelectronics, photonics, flexible electronics, optical devices, transparent electrically conductive films, displays and solar cells or as thermally conductive fillers, biotechnology, biosensors, detergents, filtration, household cleaning, rubber and plastic recycling, and or separation applications.
25. A functionalised powder obtainable by the method in accordance with any one of claims 1 to 16.
26. A method as hereinbefore described with reference to the drawings.





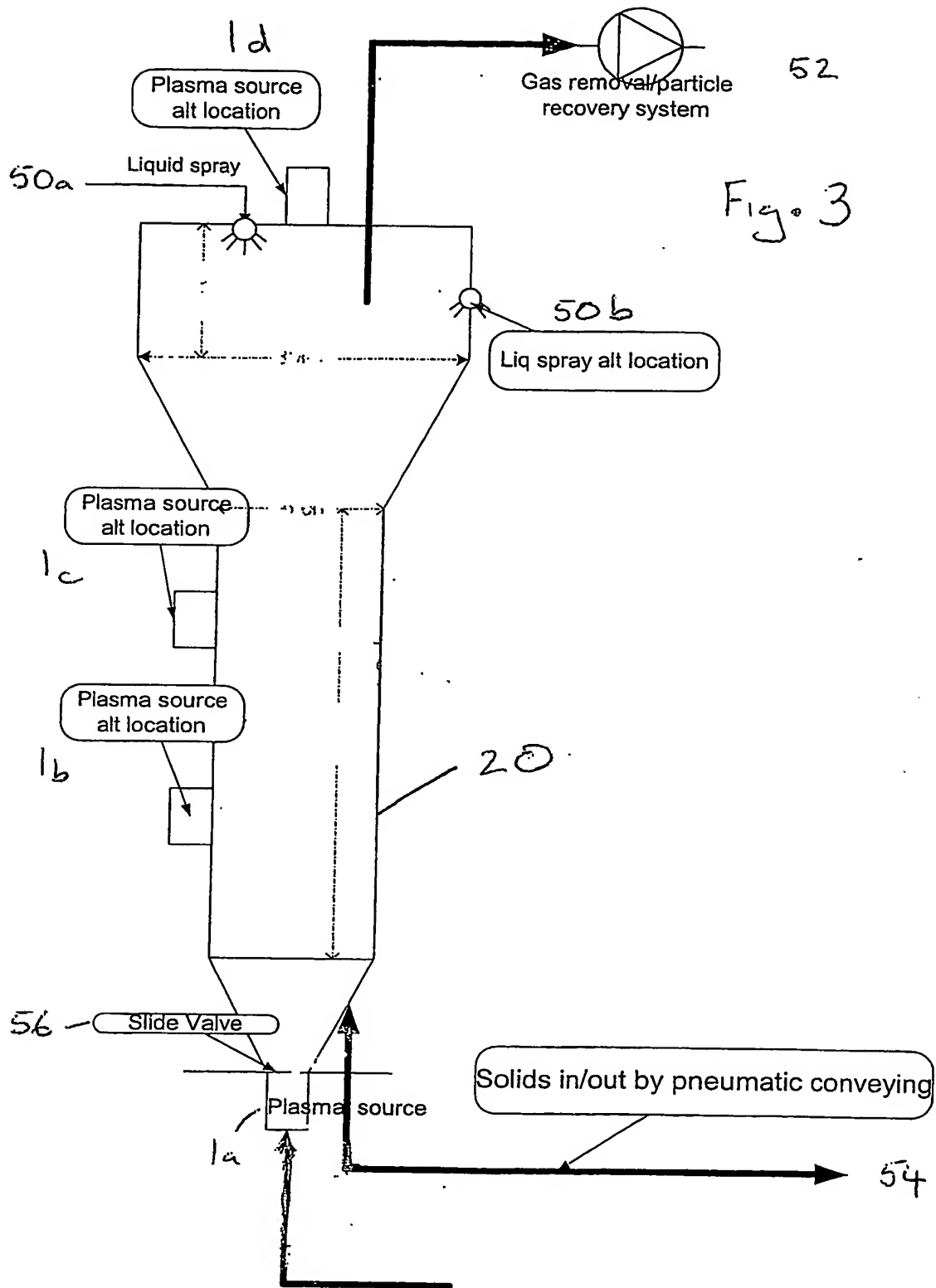


Fig. 3

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